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# TYPES OF CATALYSTSUSED INBIODIESEL PRODUCTION

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***ABSTRACT***

*A nonrenewable fuel like petroleum has been used from centuries and its usage has kept on increasing day by day. This also contributes to increased production of greenhouse gases contributing towards global issues like global warming. In order to meet environmental and economic sustainability, renewable, carbon neutral transport fuels are necessary. Transesterification is one of the most commercially useable methods to produce biodiesel and can be either carried out via non-catalytic or catalytic processes. This review article mainly focuses on types of catalysts which can be used for biodiesel production.*

***KEY WORDS:***

*biodiesel, homogeneous catalysts, heterogeneous catalysts, biocatalysts*

## INTRODUCTION

Given the potential exhaustion of traditional fossil fuels, the increasing price of petroleum, and the environment concerns, the search for alternative renewable fuels is gaining considerable attention. Biodiesel has the same properties as conventional diesel in terms of viscosity, flash point, cetane number, and many more [1].

In recent years, oil palm, algae and jatropha have been studied as potential biodiesel feedstocks. They have been found to produce much higher oil yields, compared to traditional feedstocks, such as soybean, rapeseed, sunflower, coconut, corn, cottonseed, mustard, animal fats or waste vegetable oil [2][3]. However, several other highly efficient feedstocks bear a high potential of becoming biofuels feedstocks of the future, although they have not been investigated sufficiently yet. Another prospective feedstock for biodiesel production, just emerging on the biofuels market, is camelina (*Camelinasativa),* pongamia (*Pongamiapinnata*, also called: pongam tree, karum tree and poonga-oil tree), pennycress (*Thlaspiarvense L.*), crambe – a mediterranean plant [2].

There are several methods for biodiesel production: direct use of vegetable oil, microemulsions, thermal cracking (pyrolysis), transesterification or esterification, ultrasonic reactor, microwave method, supercritical method and enzymatic method using lipase [3].

## BIODIESEL PRODUCTION

Biodiesel refers to a diesel-equivalent, processed fuel derived and ester-based oxygenated fuel from renewable biological sources. It can be made from processed organic oils and fats such as soya bean, rapeseed, sunflower, coconut, corn, cottonseed, mustard, palm oil, peanut, animal fats, waste vegetable oil and algae. In general terms, biodiesel may be defined as a domestic, renewable fuel for diesel engines which meet the requirements of ASTM D 6751. In technical terms (ASTM D 6751) biodiesel is a diesel fuel made of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated as B100 and meeting the specifications of ASTM D 6751 [3].

Biodiesel production has become an area in which many researchers have increasing interest. This is due to its potential as an alternative fuel that offers a complementary strategy for sustainability [4].

Transesterification is one of the most commercially useable methods to produce biodiesel and the process involves a reaction between ester (here triglyceride) and alcohol to form new ester and alcohol. Different types of alcohols such as, methanol, ethanol, propanol and butanol have been used. However, methanol and ethanol are the most used because of their short chains [4], particularly methanol owing to its low price and availability. In the transesterification of triglyceride to fatty acid alkyl esters three reversible reactions take place consecutively in which diglycerides and monoglycerides are major intermediate products [5]. Generally the transesterification reaction involves some critical parameters which significantly influence the final conversion and yield. The most important variables are: reaction temperature and time, free fatty acid (FFA) content in the oil, water content in the oil, type of catalyst, amount of catalyst, molar ratio of alcohol to oil, type or chemical stream of alcohol, use of co-solvent and mixing intensity [5][6]. Transesterification reaction can be either carried out via non-catalytic or catalytic processes. Non-catalytic transesterification reaction is slow and normally needs high pressures and temperatures to be completed [5]. The utilization of different types of catalysts improves the rate and yield of biodiesel [6].

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**CATALYSTS FOR BIODIESEL PRODUCTION**

Biodiesel fuel can be produced via transesterification of refined vegetable oil, waste cooking oil, and used frying oil or animal fats and its production is facilitated by using catalysts [7][8]. A catalyst is used to improve the reaction rate and yield of a reaction. There are several kinds of catalysts that can be used to produce biodiesel. It can be categorized into three main categories, i.e. homogeneous catalyst, heterogeneous catalyst and biocatalyst (enzyme) [3][4][5]. The homogeneous catalyst means the reactants and catalyst are in homogeneous stage (all in liquid form), while the heterogeneous catalyst means that the reactants and the catalyst are in different forms meaning that in the heterogeneous catalytic biodiesel production, the reactants are in liquid form and the catalyst is in solid form. There are five major types of catalyst in the biodiesel production which are homogeneous base catalyst, heterogeneous base catalyst, homogeneous acid catalyst, heterogeneous acid catalyst and biocatalyst [3][9]. The most common commercial process for biodiesel production is by homogeneous base-catalyzed transesterification of a vegetable oil with methanol [4].

**Homogeneous base catalysts**

Biodiesel is possible produce using homogeneous base catalysts, such as alkaline metal hydroxides (NaOH, KOH) [10] or alkoxides, as well as sodium or potassium carbonates [11]. Other alkoxides, such as calcium ethoxide, have also effectively catalysed biodiesel production, albeit with higher methanol and catalyst requirements [12].
These base catalysts are commonly used in the industries due to several reasons: able to catalyze reaction at low reaction temperature and atmospheric pressure, high conversion can be achieved in a minimal time, widely available and economical [10]. The homogenous base-catalyzed transesterification reaction is about 4000 times faster compared to acidic catalyst [10][12]. However, the use of this catalyst has many disadvantages such as high corrosiveness, difficulty in catalyst separation from the glycerine phase and the necessity to use a large amount of water, which, consequently, results in a considerable amount of wastewater production [4] [7]. Two of the major disadvantages of homogeneous catalysts is that they cannot be reused or regenerated [4][7], because the catalyst is consumed in the reaction, and that the separation of catalyst from the products is difficult and it requires specialized equipment, which could result in higher production costs [4]. The next disadvantages is that use of base catalyst is limited only for refined vegetable oil with less than 0.5 wt.% FFA or acid value less than 1 mg KOH/g. Some researchers ([13][14][15][16][17]) reported that base catalyst can tolerate higher content of FFA. Nevertheless, it is clear that the FFA content in oil feedstock should be as low as possible (ranging from less than 0.5 wt.% to less than 2 wt.%) for base-catalyzed transesterification reaction. Thus, if waste cooking oil with an average FFA content more than 6 wt.%, base catalyst is definitely not suitable to be used. FFA consists of long carbon chain that is disconnected from glycerol backbone. They are sometimes called carboxylic acids. If an oil or fat containing high FFA such as oleic acid is used to produce biodiesel, alkali catalyst will typically react with FFA to form soap. This reaction is highly undesirable because it will deactivate the catalyst from accelerating the transesterification reaction. Furthermore, excessive soap in the products can drastically reduce the fatty acid methyl ester (FAME) yield and inhibit the subsequent purification process of biodiesel, including glycerol separation and water washing [10].

There is a considerable number of studies on homogeneous base catalysts, e.g. KOH [18][19][20][21], NaOH [18][19][20][21][22][23], $NaOCH_3$, $KOCH_3$[18][21].

**Homogeneous acid catalysts**

Since liquid base-catalyzed transesterification process poses a lot of problems especially for oil or fat with high FFAs concentration, liquid acid catalysts (sulfuric, phosphoric, hydrofluoric, hydrochloric, alkyl benzene sulfonic, and p-toluene sulfonic acids) are proposed in order to overcome the limitations. The most investigated catalysts for acid-catalyzed system are sulfuric acid ($H_2SO_4$) and hydrochloric acid (HCl) [10]. Acid-catalyzed transesterification holds an important advantage with respect to base-catalyzed process: acid catalyst is insensitive to the presence of FFAs in the feedstock and can catalyzes esterification and transesterification simultaneously [10][12]. Esterification is a chemical reaction in which two reactants, typically an alcohol (e.g. methanol) and an acid (e.g. FFA) react to form an ester as the reaction product. It was reported that acid catalysis is more efficient when the amount of FFA in the oil exceeds 1 wt.%. In addition, economic analysis has proven that acid-catalyzed procedure, being a one-step process, is more economical than the base-catalyzed process which requires an extra step to convert FFA to methyl esters. However, acid-catalyzed system is not a popular choice for commercial applications due to slower reaction rate, requirement of high reaction temperature, high molar ratio of alcohol to oil, separation of the catalyst, serious environmental and corrosion related problem [3][10].

There are a several studies on homogeneous acid catalysts, e.g. sulfuric acid [23][24][25], phosphoric acid, trichloroacetic acid and methanesulfonic acid [24].

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**Homogeneous acid and base-catalyzed transesterification: two steps**

Since homogeneous acid and base catalysts have their own advantages and limitations, some studies ([23][26][27][28][29][30][31][32]) have attempted to use a combination of both catalysts to synthesis biodiesel from oil containing high FFAs.
A two-step process which involves acid-catalyzed transesterification process and followed by base-catalyzed transesterification process is used in converting vegetable oil with high FFA value. The first step is acid esterification and pretreatment to remove FFA in the oil, which is mainly a pretreatment process and could reduce the FFA [29]. The disadvantage of this two-step process is even more pronounced due to the requirement of extra separation steps to remove the catalyst in both stages. Problem of catalyst removal from the first stage can be avoided by using base catalyst from the second stage through neutralization process. The use of extra base catalyst will be biodiesel production more expensive.

**Heterogeneous base catalysts**

Heterogeneous base catalysts have been developed and used as the alternative catalysts, offering several advantages in overcoming the problems associated with homogeneous base catalysts [4][7]. Unlike homogeneous, heterogeneous catalysts are environmentally benign and could be operated in continuous processes [5]. The heterogeneous catalysts are not consumed or dissolved in the reaction and therefore can be easily separated from the products. As a result, the products do not contain impurities of the catalyst and the costs of final separation are reduced. These catalysts can be easily regenerated and reused and are environmentally friendlysince there is no need of a water treatment to be conducted in the separation step [4][5]. This reduction in cost is sufficient to make the biodiesel competitive with the fossil diesel because it simplifies the processing of reaction products (washing, separation and purification) and there is no occurrence of soap formation due to the neutralization of FFA or saponification of triglycerides [4]. However, a high molar ratio of alcohol to oil, large amount of catalyst and high temperature and pressure are required when utilizing heterogeneous catalyst to produce biodiesel [5].
To date, many solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides and hydrotalcites. On top of that, alkaline earth metal oxides especially calcium oxideCaO have attracted much attention due to their relatively high basic strength, low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide [10].
Applications of heterogeneous base catalysts for biodiesel production have been reviewed by a variety of researchers, e.g. CaO[33][34][35][36], $CaCO_3$[33], $Ca(OH)_2$[33][37], $Ba(OH)_2$, $Ca(MeO)_2$ [37], MgO[10][37], $K_2CO_3$ supported on MgO [38], SrO[39], metal oxide ($CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, $CaO–CeO_2$) [40], Mg/Zr catalyst [41], NaX zeolite loaded with 10 % KOH [42], ZnO-$La_2O_3$ [43], $Sr(NO_3)_2$/ZnO[44].

**Heterogeneous acid catalysts**

The emergence of applicable heterogeneous acid catalysts opens the platform for usage of low quality feedstock and as it makes up a major portion of the biodiesel production cost. This is because the usage of conventional basic catalysts for biodiesel production from low quality oils (high FFA and moisture content) are faced with the problems of soap formation and difficulty in product separation [45].
The advantages of using solid acid catalyst are: they are insensitive to FFA content, esterification and transesterification occurs simultaneously, eliminate the washing step of biodiesel, easy separation of the catalyst from the reaction medium, resulting in lower product contamination level, easy regeneration and recycling of catalyst and reduce corrosion problem, even with the presence of acid species [3][10]. In fact, the development of heterogeneous catalyst system holds an important factor to be incorporated into a continuous flow reactor. Such continuous process can minimize product separation and purification costs, making it economically viable and able to compete with commercial petroleum-based diesel fuel [10]. On the other hand, heterogeneous acid catalysts have also some disadvantages: complicated catalyst synthesis procedures lead to higher cost and longer processing time, it requires higher reaction temperature and higher alcohol to oil molar ratio and longer reaction time, required more energy, leaching of catalyst active sites may result in product contamination [3].
There are studies on heterogeneous acid catalysts, e.g.zirconium oxide ($ZrO_2$) [46], zeolites [47], catalyst RHC–$SO_3H$ prepare by sulfonating rice husk char (RHC) with concentrated sulfuric acid [1], zungstated zirconia, sulfated tin oxide, sulfated zirconia [48].

**Biocatalyst**

Enzymatic transesterification is, therefore, an attractive method for biodiesel production over chemical methods because of the reduced feedstock limitations, downstream processing and environmental impact. The use of biocatalyst (enzyme catalysts) eliminates these problems associated with acid and base catalysts as well as presents other production benefits.

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Unlike the base catalysts, biocatalyst do not form soaps so there is no restriction on FFA content. Unlike the acid catalysts, biocatalysts are not severely inhibited by water, so there is little concern about water production. Since the biocatalysts are capable of completely converting FFA to FAAEs, low cost feedstocks such as waste oils and lard can be used. The biocatalysts are most often immobilized when used, which simplifies the separation of products, produces a high quality glycerol and allows for the reuse of the catalyst [5][10][49]. These advantages prove that enzyme catalysed biodiesel production has high potential to be an eco-friendly process and a promising alternative to the chemical process. However, it still has its fair share of constraints especially when implemented in industrial scale such as high cost of enzyme, slow reaction rate and enzyme deactivation [5][10].
Applications of biocatalysts for biodiesel production have been reviewed by a variety of researchers [50][51][52][53].

## CONCLUSION

Transport has become an indispensable part of human life and also humanity has become dependent on transport. Biodiesel, as an alternative fuel for internal combustion engines, is non-toxic, biodegradable and environmentally safe (does not contribute net carbon emission to the atmosphere). Biodiesel can be produced with several methods from different types of feedstocks, e.g. vegetable oil, animal fat, waste vegetable oil, algae. However, the high prices of vegetable oils in the global market have sharply increased the overall biodiesel production cost and making it not economically viable as compared to petrol based diesel. Furthermore, the oils are important commodities in the human food supply chain and therefore its conversion to biodiesel in a long run may not be sustainable. Biodiesel from waste vegetable oil or algae are an alternative feedstock for biodiesel production, which does not compete with the edible materials.
Biodiesel fuel can be produced via transesterification by using catalysts, which is used to improve the reaction rate and yield of a reaction. Many different types of catalysts are used for the production of biodiesel via transesterification reaction, including homogeneous base catalyst, homogeneous acid catalyst, heterogeneous base catalyst, heterogeneous acid catalyst and biocatalyst. The homogeneous catalyst means the reactants and catalyst are in the same phase (all in liquid form), while the heterogeneous catalyst means that the reactants and the catalyst are not in the same phase, which allows the easy separation of the catalyst after the reaction.
Transesterification used a homogeneous basic catalysts shows a very fast kinetic of reaction but also a next saponification reaction that reduces the biodiesel production efficiency. To prevent the biodiesel yield loss due to the saponification reaction, oil and alcohol must be dry and the oil should have a minimum amount of FFA, less than 0.5 wt.%. Biodiesel is finally recovered by repeated washing with water to remove glycerol, soap and the excess of methanol. On the contrary, the acid transesterification allows to obtain a biodiesel production without formation of co-products. The disadvantages of using of an acid homogeneous catalysts are the corrosive and the slow reaction rate. This may be increased at high temperature and pressure, involving larger costs. Methanol and oil are poorly soluble, so the reaction mixture contains two liquid phases. Others alcohols can be used, but being more expensive. Moreover, an acid pre-treatment is often carried out in the homogeneous base-transesterification of oils having more of FFA, in order to improve the biodiesel efficiency production. Biocatalyst represents a potential solution to produce biodiesel from very low-quality triglycerides source, but in these cases the cost of the enzymes has to be considered. All these aspects suggest that an environmental friendly and cheaper biodiesel production process could be carried out using acid or basic heterogeneous catalysts or, better, heterogeneous catalyst with both acid and basic properties. They could combine the advantages of the alkaline and acid transesterifications with those of heterogeneous catalytic process. The appropriate catalyst should have high activity and selectivity, high stability, high water-tolerance, it should be inexpensive and its production process should be environmental friendly.

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